

MEMORANDUM

TO: Docket EPA-HQ-OAR-2002-0058

FROM: Peter Westlin, EPA/OAQPS/SPPD

DATE: January 20, 2011

SUBJECT: Measurement Imprecision for Carbon Monoxide

A. INTRODUCTION

EPA received many comments about the overall stringency of the carbon monoxide (CO) emission limits in the proposed boiler MACT rule. Some of the comments focused on measurement error associated with the analyzers that are used to quantify CO concentrations. This memorandum presents the findings of EPA's analysis.

B. DISCUSSION

For low CO levels measured using EPA Method 10, we reviewed the quality of the data relative to information provided for each emissions test. Method 10 is structured such that we can assess measurement data quality relative to the calibration span of the instrument (see <http://www.epa.gov/ttn/emc/promgate/method10r06.pdf> and <http://www.epa.gov/ttn/emc/promgate/method7E.pdf>). For example, the allowable calibration error, system bias, and drift requirements are directly proportional to the site-specific instrument calibration span (i.e., ± 2.0 percent of the calibration span value). For instrument calibration span values of 25 ppmv and less, the allowable calibration error, bias, or drift values are each ± 0.5 ppmv.

We can estimate the equivalent of the method detection level for a measurement with an instrumental test method (e.g., EPA Methods 3A, 6C, 7E, 10, and 25A) including the measurement of CO emissions using a square root formula and these method prescribed allowable data quality criteria. For example, in the case of a calibration span value of 25 ppmv, the square root formula (i.e., square root of the sum of the squares, or $(0.5^2 + 0.5^2 + 0.5^2)^{1/2}$) would indicate a value of 0.9 ppmv as the instrument detection level. Consistent with the

methodology we applied for non-instrumental methods, discussed in section C of this memorandum, where we established limits no less than three times the MDL, this estimated measurement error value of about 1 ppmv would translate a limit of 3 ppmv. For tests done with calibration spans of greater than 25 ppmv, the corresponding estimated measurement error would be greater. For example, the estimated measurement error using the square root formula for a calibration span of 100 ppmv would be about 4 ppmv which would translate to a limit of 12 ppmv. For a calibration span of 1000 ppmv, the estimated measurement error would be 35 ppmv or a limit of about 100 ppmv.

One outcome of this assessment is recognition that the site-specific estimated measurement errors in some cases may be higher than some of the reported levels. Therefore, for each emission test used in the MACT floor calculations we substituted the site-specific estimated measurement error for reported values below those values in order to ensure the quality of the data used to set the floors.

C. MEASUREMENT IMPRECISION AT OR NEAR THE METHOD DETECTION LEVEL

For the boiler and process heater source category, which includes many sources with emission levels at or near the method detection levels (MDLs) for the various pollutants, measurement imprecision is a significant factor that should be included in the development of emission limits for boilers and process heaters. To determine an appropriate methodology, EPA examined the contribution of test method measurement imprecision to the variability of a set of emissions data. One element of variability is associated with method detection capabilities and a second is a function of the measurement value. Measurement imprecision is proportionally highest for values measured below or near a method's detection level and proportionally decreasing for values measured above the method detection level.

The probability procedures applied in calculating the floor or an emissions limit inherently and reasonably account for emissions data variability including measurement imprecision when the database represents multiple tests from multiple emissions units for which all of the data are measured significantly above the method detection level. That is less true when the database includes emissions occurring below method detection capabilities and are reported as the method detection level values.

EPA's guidance to respondents for reporting pollutant emissions used to support the data collection specified the criteria for determining test-specific method detection levels. Those criteria insure that there is only about a 1 percent probability of an error in deciding that the pollutant measured at the method detection level is present when in fact it was absent. Such a probability is also called a false positive or the alpha, Type I, error. Because of sample and emissions matrix effects, laboratory techniques, sample size, and other factors, method detection levels normally vary from test to test for any specific test method and pollutant measurement. The expected measurement imprecision for an emissions value occurring at or near the method detection level is about 40 to 50 percent. Pollutant measurement imprecision decreases to a consistent relative 10 to 15 percent for values measured at a level about three times the method detection level.¹

Also in accordance with our guidance, source owners identified emissions data which were measured below the method detection level and reported those values as equal to the method detection level as determined for that test. An effect of reporting data in this manner is that the resulting database is truncated at the lower end of the measurement range (i.e., no values reported below the test-specific method detection level). A floor or emissions limit based on a truncated database or otherwise including values measured near the method detection level may not adequately account for measurement imprecision contribution to the data variability. That is, an emission limit set based on the use of the MDL to represent data below the MDL may be significantly different than the actual levels achieved by the best performing units due to the imprecision of the measurements. This fact, combined with the low levels of emissions measured from many of the best performing units, led EPA to develop a procedure to account for the contribution of measurement imprecision to data variability.

We applied the following procedures to account for the effect of measurement imprecision associated with a database that includes method detection level data. The first step is to define a method detection level that is representative of the data used in establishing the floor or emissions limit and that also minimizes the influence of an outlier test-specific method detection level value. We reviewed each pollutant-specific data set to identify the highest test-specific method detection level reported that was also equal to or less than the average emissions

¹ American Society of Mechanical Engineers, *Reference Method Accuracy and Precision (ReMAP): Phase I, Precision of Manual Stack Emission Measurements*, CRTD Vol. 60, February 2001.

level (i.e., unadjusted for probability confidence level) calculated for the data set. We believe that this approach is representative of the data collected to develop the floor or emissions limit while to some degree minimizing the effect of a test(s) with an inordinately high method detection level (e.g., the sample volume was too small, the laboratory technique was insufficiently sensitive, or the procedure for determining the detection level was other than that specified).

The second step in the process is to calculate three times the representative method detection level and compare that value to the calculated floor or emissions limit. If three times the representative method detection level were less than the calculated floor or emissions limit calculated from the upper prediction limit (UPL), we would conclude that measurement variability was adequately addressed because the measurement imprecision at that level is a consistent 10 to 15 percent. The calculated floor or emissions limit would need no adjustment. If, on the other hand, the value equal to three times the representative method detection level were greater than the UPL-based emission limit, we would conclude that the calculated floor or emission limit does not account entirely for measurement variability. If indicated, we substituted the value equal to three times the representative method detection level to apply as the adjusted floor or emissions limit. This adjusted value would ensure measurement variability is adequately addressed in the floor or the emissions limit.